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Limestone fluidized bed treatment of acid-impacted water at the Craig Brook National Fish Hatchery, Maine, USA

Philip L. Sibrell [a,*], Barnaby J. Watten [a], Terry A. Haines [b], Benjamin W. Spaulding [c]

[a] *United States Geological Survey, Leetown Science Center, 11649 Leetown Rd., Kearneysville, WV 25430, USA*

[b] *United States Geological Survey, Leetown Science Center, Orono Field Station, 5751 Murray Hall, University of Maine, Orono, ME 04469-5751, USA*

[c] *Department of Biological Sciences, University of Maine, 5751 Murray Hall, Orono, ME 04469-5751, USA*

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Abstract

Decades of atmospheric acid deposition have resulted in widespread lake and river acidification in the northeastern U.S. Biological effects of acidification include increased mortality of sensitive aquatic species such as the endangered Atlantic salmon (*Salmo salar*). The purpose of this paper is to describe the development of a limestone-based fluidized bed system for the treatment of acid-impacted waters. The treatment system was tested at the Craig Brook National Fish Hatchery in East Orland, Maine over a period of 3 years. The product water from the treatment system was diluted with hatchery water to prepare water supplies with three different levels of alkalinity for testing of fish health and survival. Based on positive results from a prototype system used in the first year of the study, a larger demonstration system was used in the second and third years with the objective of decreasing operating costs. Carbon dioxide was used to accelerate limestone dissolution, and was the major factor in system performance, as evidenced by the model result: $\text{Alk} = 72.84 \times P(\text{CO}_2)^{1/2}$; $R^2 = 0.975$. No significant acidic incursions were noted for the control water over the course of the study. Had these incursions occurred, survivability in the untreated water would likely have been much more severely impacted. Treated water consistently provided elevated alkalinity and pH above that of the hatchery source water.

Keywords: Acid; Limestone; Alkalinity; Atlantic salmon; Aluminum; Hatchery

1. Introduction

Acidic rain and snowmelt are impacting freshwater streams and rivers in many regions of the country, particularly in New England, where soil buffering

* Corresponding author. Tel.: +1 304 724 4426; fax: +1 304 724 4428.

E-mail address: psibrell@usgs.gov (P.L. Sibrell).

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capacity is low. For example, at the Craig Brook National Fish Hatchery, in East Orland, Maine, one of two federal hatcheries constructed for the conservation of endangered Atlantic salmon (*Salmo salar*), inlet water alkalinity is less than 10 mg/L as $CaCO_3$, and inlet pH often drops below 6.0. The low pH and dissolved aluminum associated with acidified water affect fish through ion regulation and gill function (Staurnes et al., 1996). Atlantic salmon are especially susceptible to acid/aluminum exposure during the smoltification process when physiological changes associated with migration to the salt-water environment are taking place. Under these conditions, as little as 30 μg/L aluminum in the labile or free state can inhibit the smoltification process thus impacting seawater survival (Kroglund and Staurnes, 1999). Aluminum toxicity can be decreased by increasing the pH, which shifts the aluminum ion speciation to a less toxic form. A method of increasing the pH and alkalinity of water sources would therefore decrease toxicity and increase survival of this endangered species. Conventional methods of alkalinity adjustment, such as the addition of sodium bicarbonate, would be uneconomic considering the large volumes of water requiring treatment. Economic analysis of reagents for acid neutralization indicates that the least expensive form of alkalinity is calcium carbonate or limestone (Hedin et al., 1994). However, the dissolution rate of limestone is generally not rapid enough to conveniently treat the high volumes of water required. Recent research at the Leetown Science Center of USGS has shown that limestone reactivity can be enhanced by the addition of carbon dioxide (CO_2) to water before contact with limestone. This technology has been utilized in the treatment of acid mine drainage (Watten, 1999; Sibrell et al., 2000) and has demonstrated the enhancement of the limestone dissolution rate. An additional benefit of limestone use is the increase in dissolved calcium concentration, which has been shown to be beneficial to fish exposed to acidic environments (Leivestad, 1989). The purpose of this paper is to describe the development and operation of a CO_2-enhanced fluidized limestone bed reactor for alkalinity-enhancement of acid-impacted water. Because of the volume of the lakes and ponds which serve as the source for the Craig Brook hatchery, the water at the Craig Brook facility is not as severely impacted by acid precipitation as other streams and rivers in the region; but it is believed that the results of this investigation will be applicable to more severely affected waters as well.

2. Methods

Testing of the alkalinity-enhancement system was conducted at the Craig Brook National Fish Hatchery in East Orland, Maine. Water for hatchery operations at this location was supplied from three different sources. The primary source was Craig Pond, but water was also obtained from Alamoosook Lake and from groundwater. Each of these water inputs has limited alkalinity of less than 10 mg/L $CaCO_3$ equivalent.

2.1. Prototype treatment system

The alkalinity of hatchery water was increased by contacting source water with limestone in a sealed fluidized bed reactor. The prototype treatment system used in year one of the study had a treatment capacity of 12 L/min water flow, and consisted of a 10-cm packed column for adsorption of CO_2 into water (the carbonator), followed by a 15-cm column that served as a fluidized bed reactor for the dissolution of limestone (generally as shown in Fig. 1 except that sand filters were not present in the prototype system). Both columns were 1.5 m tall. A 220 W centrifugal pump was used to boost the inlet pressure of the water to maintain constant flow into the pressurized carbonator column. Water treatment flow rate was monitored using a paddlewheel flow sensor connected to a battery-operated flow meter and accumulator. The CO_2 source was an insulated Dewar cylinder containing approximately 180 kg of liquid CO_2, which was replenished as required by the vendor. Carbon dioxide flow into the system was monitored using a Brooks Sho-Rate model 1350 variable area flow meter with a needle valve for flow regulation.[1] The manufacturer provided a calibration chart giving CO_2 flow in standard liters per minute (SLPM) at the ambient temperature and delivery pressure as a function of the

[1] Any use of trade, product or firm names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

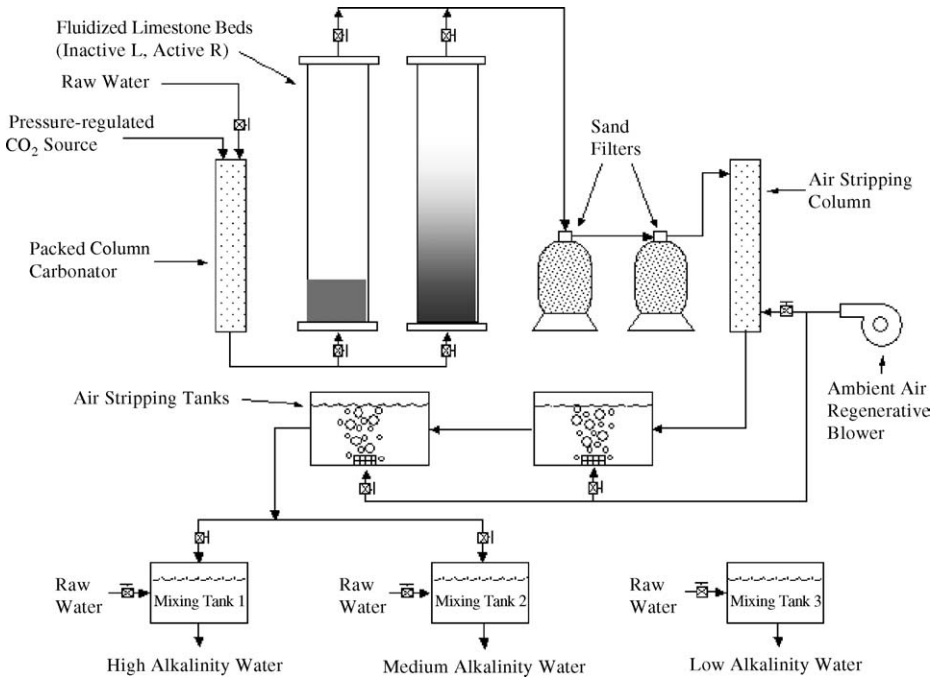

Fig. 1. Schematic of alkalinity-enhancement treatment system. Prototype system did not have sand filters as shown, but is otherwise similar.

flow meter reading. Effluent alkalinity was controlled by varying the CO_2 input rate.

Excess CO_2 was removed from the treated water using a 10-cm diameter packed tower scrubber, followed by air sparging using eight air diffusers in an insulated, baffled tank with a residence time of 7 min. The column packing in both the carbonator and stripper consisted of 2.5-cm Pall rings. Initially, a 200 W regenerative blower was used to direct air through the stripping column and into the stripping tank. The 200 W blower was replaced by a larger 400 W blower to increase performance later in year 1. Based on blower performance curves at a pressure drop of 5 kPa, the increased blower size tripled the stripping air flow rate, from about 400 to over 1200 L/min. The treated water from the system was used to prepare the high and medium alkalinity water by mixing with untreated water in insulated tanks. After mixing and dilution, 22 L/min of each water type was available for use. The three resulting water types: untreated, medium alkalinity and high alkalinity were then piped to the appropriate egg trays, fry troughs or grow-out tanks. Water temperature was monitored upstream and downstream of the limestone system. The system was installed in January and February of 1999, and performance tests were conducted from March through April at water temperatures of $5 \pm 2\ ^{\circ}C$. Following initial performance tests, the system was used to supply water for fish culture, from May through September. During this time, the limestone columns were replenished every 3–4 days, to replace limestone dissolved in the treated water. The effect of limestone bed depth was evaluated in May and June, with water and CO_2 flow rates held constant, at 9.5 L/min and 2.5 SLPM, respectively.

2.2. Demonstration treatment system

For years two and three of the study, a larger water treatment system (Fig. 1) was built to demonstrate the process and test the economics of alkalinity-enhancement. This was accomplished by increasing the diameter of the limestone fluidized bed reactors from 15 to 30 cm. These reactors were purchased commercially (Aquatic Eco-Systems Inc., Quiksand™ Fluidized Bed Biofilters, part number FB93) to minimize assembly time. A second set of 15-cm Fluidized Bed Biofilters (Aquatic Eco-Systems Inc., part number

Table 1
Particle size distributions of limestone used in years 2 and 3

Screen (mesh)	Diameter (μm)	Year 2		Year 3	
		wt.% retained	Cum. wt.% retained	wt.% retained	Cum. wt.% retained
30	600	25.4	25.4	32.4	32.4
40	425	28.6	54.0	20.1	52.5
50	300	20.1	74.1	15.3	67.8
70	212	13.7	87.7	12.6	80.4
100	150	7.8	95.5	9.3	89.6
Pan	<150	4.5	100.0	10.4	100.0

FB91) served as the carbonator and stripping columns in the enlarged system. The height of the carbonator and stripping columns was 178 cm, whereas the fluidized bed columns were 203 cm tall. The greater size of the reactors allowed a longer period between recharging, up to 14 days, thus reducing the labor involved in operating the treatment system. The CO_2 stripping capacity was also increased by addition of a second air sparged, insulated tank in series with the first to provide a total residence time of 4 min. The water booster pump and regenerative blower were upgraded to 400 and 750 W, respectively. These changes enabled an increase in the treated water flow rate to 38 L/min. After mixing and dilution, 45 L/min of water at each of the high, medium and control levels of alkalinity was available for use. Influent water and CO_2 flows were measured as before, using the instrumentation transferred from the prototype unit. System performance was characterized in November of 2000, where effluent alkalinity was measured as a function of CO_2 input, with water flow rate and limestone bed depth held constant, at 38 L/min and 20–25 cm, respectively. Water temperature was 9 °C for the duration of this test series. This system was used to supply water for fish culture during years 2 and 3, under constant operating conditions. The larger system was also modified to prevent carryover of fine limestone particulates from the limestone columns. This was accomplished by the addition of two pressurized sand bed filters operating in series. The filters were purchased commercially (Aquatic Eco-Systems Inc., Tagelus Sand Filter, part number TA35), with a capacity of 45 kg of sand, and a maximum treatment capacity of 130 L/min. The first filter was filled with Aquatic Eco-Systems Inc. Mixed Media (part number MM1), and the second filter filled with locally available sand. Filters were briefly bypassed and backwashed when pressures rose above 100 kPa.

Proper performance of the fluidized bed reactor was dependent upon the particle size distribution of the limestone. The limestones had to be coarse enough to resist being swept out of the reactor, and yet fine enough to be fluidized by the water flow. Limestone was obtained from the Bellefonte Lime Company as high calcium glass sand, with a $CaCO_3$ content of 96.5%. Minor impurities associated with the limestone were magnesium carbonate and insolubles such as silica. Particle size distributions for the limestone used in years 2 and 3 are shown in Table 1. As the limestone was consumed during operation, the depth of the fluidized bed in the reactor decreased. Makeup limestone was added every 3–4 days for the prototype system, and every 7–14 days for the demonstration system. This was typically done when product water alkalinity fell below about 100 mg/L. At that point, flow was diverted to an identical column with a fresh charge of limestone so that no interruption of flow occurred. This enabled production of treated water to continue while the first column was recharged with limestone. After recharging, the limestone was rinsed overnight to wash out fine particles.

Water acidity and alkalinity were measured approximately daily using standard titration methods (APHA, 1995). Water pH was measured with either an Orion SA 250 or 210A portable pH meter, each equipped with an Orion Ross electrode.

3. Results and discussion

As a carbonate mineral, limestone is strongly affected by the partial pressure of CO_2 [$P(CO_2)$]. The kinetics of limestone dissolution has been explored in

detail by Plummer et al. (1978). They defined three possible mechanisms for the dissolution of limestone:

$$CaCO_3 + H^+ = Ca^{2+} + HCO_3^- \quad (1)$$

$$CaCO_3 + H_2O + CO_2 = Ca^{2+} + 2HCO_3^- \quad (2)$$

$$CaCO_3 + H_2O = Ca^{2+} + HCO_3^- + OH^- \quad (3)$$

These mechanisms were termed attack by acid, CO_2 and water, respectively. Under certain conditions of pH and $P(CO_2)$, one or another of these mechanisms may be dominant. The total dissolution rate is the sum of these three mechanisms. Combining Eqs. (1)–(3), Sverdrup (1985) developed an overall kinetic expression for calcite particles >10 μm:

$$-\frac{dm}{dt} = [k_1[H^+] + k_2[CO_2] + k_w - k_b([Ca^{2+}][HCO_3^-])] \times \frac{3m}{\rho r} \quad (4)$$

where [ ] refers to the bulk solution concentration, k_1 and k_2 are the first-order reaction constants, k_w the zero-order constant for Eq. (9), k_b the constant for the backward reaction driven by the interaction of Ca^{2+} and HCO_3^- with calcite, m the mass of particle, ρ the density of the limestone and r is the particle radius. Inspection of Eq. (4) shows that calcite dissolution is accelerated under conditions of low pH, high free carbon dioxide concentrations, high turbulence and when particle size (r) is small. Fig. 2 shows the contributions of each of the mechanisms as a function of $P(CO_2)$. The rates were calculated based on rate constants determined experimentally by Plummer et al. (1978), for water at 10 °C. The rate of reaction (3) is not affected by $P(CO_2)$, so it appears as a horizontal line on the plot, fixed only by temperature. The rate of CO_2 attack, reaction (2), increases with $P(CO_2)$, and exceeds the water rate at a pressure of about 14 kPa. The acid attack rate, reaction (1), is alsoaffected by $P(CO_2)$, since CO_2 is a weak acid, through a shift of the pH to lower levels as $P(CO_2)$ increases. Under the conditions given, however, this mechanism does not contribute significantly to the overall dissolution rate. The net effect of CO_2 addition is an increase in dissolution rate above $P(CO_2)$ of 0.7 kPa, with a doubling of the rate at 14 kPa, and an enhancement of up to 10 times the water rate at 140 kPa CO_2.

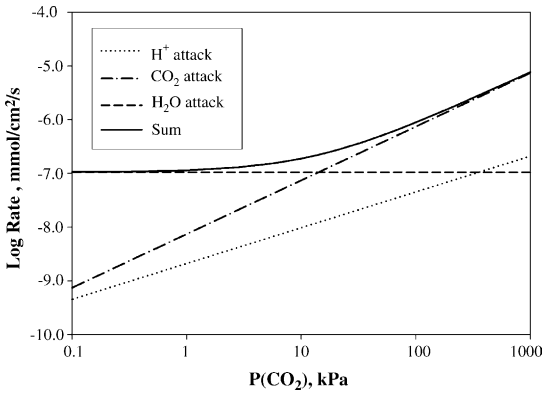

Fig. 2. Effect of CO_2 partial pressure [$P(CO_2)$] on dissolution rate of limestone at 10 °C through mechanisms of acid, CO_2 and water attack.

3.1. Prototype treatment system

The prototype alkalinity-enhancement system was installed at the Craig Brook hatchery in January of 1999. System performance was evaluated over the next several weeks. Fig. 3 shows the effect of $P(CO_2)$ in the carbonator on treatment system effluent alkalinity. The CO_2 partial pressure was calculated using the Henry's law constant for CO_2 at the temperature of the water to convert the inlet concentration of CO_2 to pressure. Also shown in Fig. 3 is the equilibrium concentration of alkalinity as a function of CO_2 pressure, as predicted

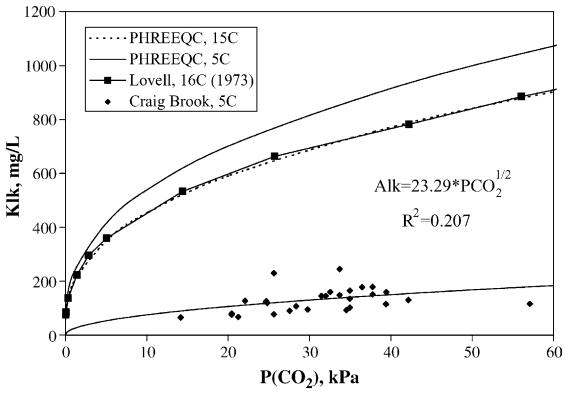

Fig. 3. Effect of CO_2 partial pressure [$P(CO_2)$] on effluent alkalinity (Alk) of prototype system at 5 °C. Geochemical modeling results (PHREEQC) also shown for 5 and 15 °C as well as experimental equilibrium dissolution data at 16 °C.

using the geochemical modeling program PHREEQC (Parkhurst, 1995). The temperature effect is shown by the PHREEQC model results at 5 and 15 °C, as an increase in alkalinity as the temperature decreases. The solubility of CO_2 in water increases as the temperature decreases (Colt, 1984), which accounts for the increase in alkalinity predicted. Also shown are experimental data from Lovell (1973) that confirm the geochemical model results at 16 °C. Although theoretical considerations lead to a cube root dependence of alkalinity on CO_2 pressure (Stumm and Morgan, 1996), previous experience with CO_2-enhancement with acid mine drainage systems has shown that a square root dependence fits the data adequately, with the advantage that the square root form is more easily handled for subsequent modeling of the system performance (Watten et al., 2004). Therefore, the performance of the prototype system was fitted to a square root dependence on CO_2 pressure, with the result:

$$\text{Alk} = 23.29 \times P(\text{CO}_2)^{1/2}; \qquad R^2 = 0.207 \qquad (5)$$

It is apparent that the system is operating well below the equilibrium level. This is most probably because of the limited contact time between the water and the limestone in the fluidized bed system, which at a rate of about 12 L/min gives a contact time of less than 2 min. The resulting alkalinity showed a slight upward trend with increasing CO_2 pressure, but not as strongly as the model would have suggested. However, there was considerable scatter in the data, which may be due to variations in the limestone bed depth, or the weight of limestone in the reactor, from test to test.

Although these results show that limestone dissolution can be increased by CO_2 addition, CO_2 is much more expensive than limestone. Therefore, the effect of increasing the weight of limestone in the reactor, which has the effect of increasing contact time and the limestone surface area, was investigated. The effect of limestone addition was followed through the limestone settled bed depth, and was investigated with all other variables held constant. The results (Fig. 4) show increasing limestone dissolution as bed depth increased, as expected. A curve has been fitted to the data in Fig. 4 that conforms to the physical constraints that no alkalinity change will be experienced for a bed depth of zero, while the bed depth effect should level off at higher limits because of back reaction kinetics.

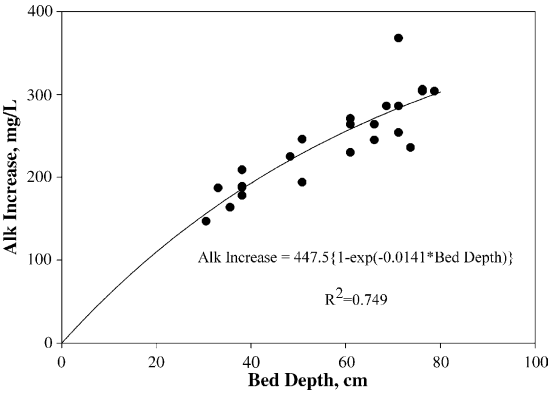

Fig. 4. Effect of limestone bed depth on increase in effluent alkalinity (Alk) for prototype system.

The result is:

$$\text{Alk increase} = 447.5 \times \{1 - \exp(-0.0141 \times \text{bed depth})\}; \quad R^2 = 0.749 \qquad (6)$$

Physical limitations such as the depth of limestone that can be fluidized by the system also exist. In further testing, the limestone bed depth was held at as high a level as practical to maximize limestone dissolution.

Although CO_2 has a beneficial effect on the extent and rate of limestone dissolution, it also has adverse physiological effects on fish and other aquatic organisms (Ross et al., 2001). Therefore, the CO_2 must be removed from the water before use in hatchery operations. Based on a water flow [$Q(H_2O)$] of 12 L/min, and CO_2 flow [$Q(CO_2)$] of 2–6 SLPM, CO_2 concentrations in the treated water can range from 300 to nearly 1000 mg/L. Initially, stripping was accomplished in the year 1 prototype using a 200 W regenerative blower to direct air through the stripping column and air sparged tank. However, residual CO_2 concentrations after stripping were above the recommended limit of 10 mg/L for fish culture (Piper et al., 1982; Ross et al., 2001). A larger, 400 W air blower was installed at this point to improve stripping performance. Dissolved CO_2 measurements were made for the effluents from the limestone column, the stripping column, and the sparged ice chest, both before and after the blower upgrade. Results are shown in Table 2. The greater air-to-liquid volume ratio obtained with the larger blower resulted in removal of CO_2 to levels well below the recommended limit of 10 mg/L for fish culture.

Table 2
Carbon dioxide stripping performance—effect of blower size on CO_2 removal in prototype system

$Q(H_2O)$ (L/min)	$Q(CO_2)$ (SLPM)	Alk (mg/L)	Blower (W)	CO_2 concentration (mg/L)		
				Column	Tower	Chest
9.5	5.28	115	200	761	198	20
11.4	3.99	120	200	378	198	75
10.2	4.52	142	400	695	194	5.3
9.5	2.49	NA	400	400	122	0.8

NA, not analysed.

For the duration of year 1 activities, the system was run under the standard conditions of 9.5 L/min water flow, 2.5 SLPM of CO_2 flow and 30–80 cm of limestone bed depth. This typically produced 9.5 L/min of water with an alkalinity of 150–250 mg/L for dilution and preparation of the medium and high alkalinity treatments. Some variability is inevitable in the treated water alkalinity because of limestone consumption within the fluidized bed and eventual depletion and subsequent recharging of the bed. Table 3 shows the mean, standard deviation, minimum and maximum for each of the three water treatment levels. The minimum pH observed during the season in the control water was 5.00. The minima in the medium and high alkalinity waters were 6.50 and 6.70, respectively. Thus, despite the variability in alkalinity in the treated waters, the treatment system effectively prevented low pH excursions known to be harmful to fish health and survival.

3.2. Demonstration treatment system

Based on the positive results from year 1 of the study, a larger treatment system was built in year 2 with the objective of decreasing labor and CO_2 requirements for the alkalinity-enhancement process. The system was designed to produce twice the amount of water available at each of the three alkalinity levels, after dilution and mixing of the system effluent. Performance testing of the system was conducted in November 2000, to determine the effect of CO_2 addition on the product water alkalinity. The results of that test are shown in Fig. 5, again as a function of $P(CO_2)$ in the water leaving the carbonator. Note that much lower CO_2 pressures were attained with the large system, because of the much greater water flow. The performance curve was again modeled with a square root dependence on the CO_2 partial pressure, with the result:

$$\text{Alk} = 72.84 \times P(\text{CO}_2)^{1/2}; \qquad R^2 = 0.975 \tag{7}$$

The model coefficient for the demonstration system is approximately three times that of the prototype system, and illustrates the increased performance characteristics of the larger system. Also shown in Fig. 5 are the results of PHREEQC modeling runs that describe the amount of alkalinity that would be added

Table 3
Water quality statistics for years 1–3

Year	Treatment	Alkalinity (mg/L)				pH			
		Mean	S.D.	Minimum	Maximum	Mean	S.D.	Minimum	Maximum
1998–1999	Control	7.0	1.8	2.0	11.0	6.50	0.38	5.00	7.30
	Medium	31.6	6.7	20.0	55.0	7.21	0.28	6.50	7.80
	High	53.1	10.3	30.0	83.0	7.38	0.24	6.70	8.00
1999–2000	Control	7.8	1.6	4.0	15.0	6.35	0.29	5.40	7.80
	Medium	35.6	5.0	21.0	50.0	7.17	0.25	6.10	8.10
	High	58.2	8.0	30.0	80.0	7.46	0.22	6.70	8.40
2000–2001	Control	7.9	1.5	5.0	13.0	6.22	0.20	5.90	6.80
	Medium	33.2	4.6	24.0	53.0	6.88	0.34	6.10	7.70
	High	54.6	7.4	45.0	80.0	7.16	0.37	6.40	7.90

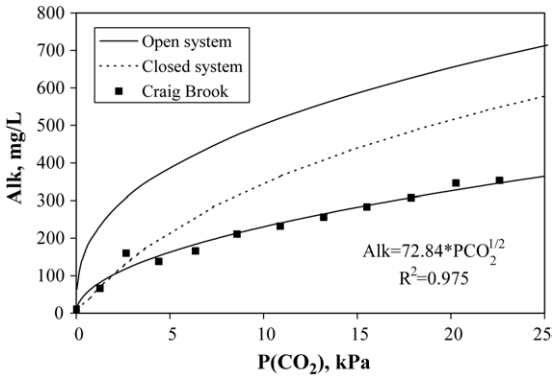

Fig. 5. Effect of CO_2 partial pressure [$P(CO_2)$] on effluent alkalinity (Alk) of demonstration system at 9 °C. Geochemical modeling results shown for open and closed systems, also at 9 °C.

to the water when in equilibrium with limestone and CO_2. The model runs were calculated for a water temperature of 9 °C, which was equivalent to the hatchery water temperature at this time. The upper curve represents the equilibrium response of an open system, where the water and limestone are exposed to a reservoir at constant pressure of CO_2, and is calculated similarly to that shown in Fig. 3. However, this does not represent actual conditions in the fluidized bed system. Here, the CO_2 is added before the water is introduced into the limestone column, and is not replenished during reaction with the limestone. Under these conditions, some of the CO_2 is converted to bicarbonate (Eq. (2)), and therefore the CO_2 concentration is depleted. This result is sometimes described as a closed system. The intermediate curve on Fig. 5 represents the model results for a closed system, and shows a decrease in expected effluent alkalinity because of CO_2 depletion. The actual performance of the system is below this level over most of the range tested, except at low $P(CO_2)$. As $P(CO_2)$ increases, more limestone must dissolve to reach the equilibrium concentration. The retention time of the water in the large system was about the same as in the prototype, at less than 2 min exposure to the limestone in the fluidized bed. Given a fixed contact time, the net effect is a greater negative deviation from the equilibrium line as CO_2 is increased. Thus, as CO_2 input increases, more and more of the CO_2 sent into the system simply passes straight through, without conversion to bicarbonate or alkalinity. This waste of a valuable resource also increases the load on the stripping system. Therefore, the system operates most efficiently at lower CO_2 levels, where equilibrium is reached more rapidly, in this case, at about 2–5 kPa CO_2.

Table 3 shows the statistics for each of the three alkalinity levels produced by the system during years two and three. Note that the minimum pH observed in the alkalinity treatments was well above the control. This alkalinity represents buffering capacity that is available should acid precipitation events impact the hatchery water supply. Also, because limestone was used as the alkalinity source, calcium was added to the water by the alkalinity-enhancement process, at the rate of 4 mg/L per every 10 mg/L alkalinity as $CaCO_3$. Mortalities for years 2 and 3 for all three alkalinity levels were below the normal rate of 40% to the swim-up stage for the Craig Brook Hatchery (Dr. Terry A. Haines, University of Maine, Orono, ME, USA, unpublished data). Had the hatchery water supply experienced a significant acid surge due to rapid snowmelt or precipitation runoff, mortalities for the control treatment may have been much larger, and the protective effect of the alkalinity-enhancement system much more dramatic.

3.3. Process economics

The increase in treatment rate for the large system allowed for a lower target alkalinity in the product water, with the result that the CO_2 addition could be lowered, thus increasing the efficiency at which the CO_2 was used. This translates to a savings in operating costs, as CO_2 was one of the most costly inputs into the alkalinity-enhancement process. Capital and operating costs (in 1999 dollars) for the large-scale system are given in Table 4. The capital cost was about US$ 8000. The treatment capacity of the system for testing was 45 L/min of each of three different water alkalinity levels. If the system were dedicated to producing water with an alkalinity of about 20 mg/L, the capacity of the system would be about 480 L/min. The Craig Brook hatchery total flow is on the order of 5000 L/min, so the system would require significant scale-up, which would increase the cost of the treatment system, but would also probably improve the cost efficiency of the system. Operating costs for year-round water treatment were calculated to be about US$ 6000/year, with about one half of that cost due to labor associated with monitoring system performance, backwashing the sand filters and

Table 4
Capital and operating costs for alkalinity-enhancement demonstration treatment system with a capacity of 38 L/min

Item	Description	Unit cost (US$)	Quantity	Total cost (US$)
(A) Capital costs				
1	30 cm diameter fluidized bed column	1020	2	2040
2	15 cm diameter carbonator column	595	1	595
3	15 cm diameter scrubber column	595	1	595
4	Column packing	80	–	80
5	150 L ice chest scrubber	231	2	462
6	20 L mixing coolers	20	3	60
7	0.75 kW regenerative blower	539	1	539
8	1 in. centrifugal pump	409	2	818
9	Flow sensor and meter	960	1	960
10	Pressure gauge	33	1	33
11	Pipe, valves and fittings	600	–	600
12	CO_2 regulator and flowmeter	200	1	200
13	Sand filter and media	250	2	500
14	Air stones	7	16	118
	Total			7600

Item	Description	Unit cost (US$)	Quantity	Annual cost (US$)
(B) Operating costs				
1	Limestone	55 tonne^{-1}	2 tonnes/year	110
2	Electricity	0.12 kWh^{-1}	26.4 kWh/day	1160
3	CO_2	0.40 kg^{-1}	7.1 kg/day	1040
4	Tank rental	1.00 day^{-1}	–	365
5	Labor	15.84 h^{-1}	4 h/week	3295
	Total			5970

refilling the limestone in the fluidized bed reactor. Seasonal use, timed to correspond with spring snowmelt and higher likelihood of acid events, would decrease operating costs substantially. Limestone material costs were low, but could be impacted by shipping costs depending on the distance to an appropriate supplier. Carbon dioxide costs were the largest material cost.

3.4. CO_2 recycle

A trade-off in operating and capital costs could be realized by installing gas stripping and absorption columns to recycle CO_2 from the treated water to incoming water. The effect of gas recycle can be predicted based on a mass balance on the CO_2 entering and leaving the reactor:

$$[CO_2]_{effluent} = [CO_2]_{influent} + [CO_2]_{added} - [CO_2]_{alkalinity} \quad (8)$$

Since the water volume does not change, the mass balance can be expressed in terms of mg/L CO_2, with the CO_2 addition converted to mg/L by conversion of SLPM CO_2 to mg/min CO_2, and by dividing by the water flow rate in L/min. Generation of alkalinity consumes CO_2 by the stoichiometric ratio derived from Eq. (2), which is 0.44. Also, for the Craig Brook hatchery water, the CO_2 concentration in the influent is negligible. Therefore, solving for the addition of CO_2:

$$[CO_2]_{added} = \frac{M_{CO_2}}{L} = [CO_2]_{effluent} + 0.44 \times Alk \quad (9)$$

The concentration of CO_2 in the effluent is given by the total amount of CO_2 in the water entering the limestone column, less the CO_2 used in generation of alkalinity, times the factor $1 - E$, where E is the fraction of CO_2 returned to the influent by the CO_2 recycle loop. Also, the total amount of CO_2 in the water entering the limestone column can be expressed in terms of alkalinity using the square root fit derived

in Eq. (7).

$$\frac{M_{CO_2}}{L} = \left(\left[\frac{\text{Alk}}{72.84} \right]^2 \times z - 0.44 \times \text{Alk} \right) \times (1 - E) + 0.44 \times \text{Alk} \quad (10)$$

The conversion factor z converts CO_2 pressure in kPa to concentration in solution, and is numerically equal to 24.12 at 9 °C. Note that this result is valid for the demonstration treatment system only, but other systems could be modeled similarly using experimentally derived coefficients for those systems. Collecting terms and simplifying gives the result:

$$\frac{M_{CO_2}}{L} = \left(\left[\frac{\text{Alk}}{72.84} \right]^2 \times z \right) \times (1 - E) + 0.44 \times E \times \text{Alk} \quad (11)$$

Eq. (11) can be rearranged and solved for alkalinity as a function of CO_2 input and recycle efficiency factor E, through use of the quadratic equation.

$$\text{Alk} = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}, \quad (12)$$

where

$$a = \frac{(1 - E) \times z}{(72.84)^2} \quad (13)$$

$$b = 0.44 \times E \quad (14)$$

$$c = \frac{-M_{CO_2}}{L} \quad (15)$$

The positive root of the quadratic is the alkalinity predicted by the model under the specified conditions. Fig. 6 shows the predicted effect of efficiency of the CO_2 recycle on product water alkalinity based on these calculations. The recycle advantage is greater at high CO_2 inputs and high recycle levels. However, even at a relatively low CO_2 pressure of 5 kPa and with 75% recycle efficiency, the model predicts an increase in effluent alkalinity from 163 to 211 mg/L, an increase of nearly 30%. Economic analysis of local factors would be required to determine the optimum trade-off between increased capital cost of the CO_2 recycling system and the decreased operating costs associated with lower and/or more efficient use of commercial CO_2.

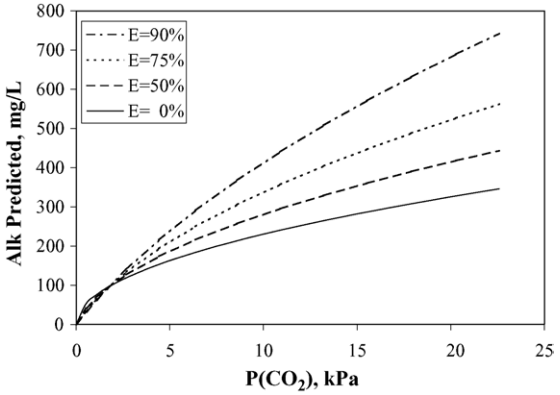

Fig. 6. Predicted effect of CO_2 recycle efficiency (E) on effluent alkalinity (Alk), based on mass balance on CO_2 entering and exiting the system at 9 °C.

4. Summary

A limestone fluidized bed reactor was tested at the Craig Brook National Fish Hatchery in East Orland, Maine, for enhancement of the alkalinity or acid neutralizing capacity of the hatchery water supply. Acidic precipitation events have the potential to seriously affect hatchery operations because of the low acid buffering capacity of the hatchery water supply. The fluidized bed reactor makes use of limestone, the most economical agent available for acid neutralization. Limestone reactivity was enhanced through the addition of CO_2 to the water before introduction to the limestone fluidized bed reactor. Several parameters affected the performance of the system, including CO_2 addition, water flow rate, and limestone bed depth or mass. Operational experience with the system has shown that CO_2 inputs were minimized by increasing reactor size and limestone contact time to more closely approach equilibrium values of alkalinity. Treated water at both the medium and high alkalinity levels had a significantly higher pH, with minimum levels of 6.0 and 6.4, respectively. Filtration of the system effluent was found to be necessary to prevent limestone fines from impacting survival of the eggs while in the egg trays. This was accomplished in the demonstration system by adding two sand filters operating in series. Genetic analysis of returning salmon is ongoing to evaluate the effect of the alkalinity treatment on the long-term survivability of the salmon. These results will be published separately

(Dr. Terry A. Haines, University of Maine, Orono, ME, USA, unpublished data). No significant acid precipitation events occurred during the course of the alkalinity-enhancement experiments. In salmon habitat where acid/aluminum exposure is more common, the effect of alkalinity-enhancement would be much greater. The major material cost for the system is the CO_2 addition, which can be managed by optimizing the treated water production rate and alkalinity to best achieve the desired alkalinity level. Carbon dioxide costs could be reduced even further by installation of a recycling system to return CO_2 stripped from the treated water back to the incoming water.

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